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Remarks:
A request for correction in the specification has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

(54) Highly active cationic ruthenium and osmium complexes for olefin metathesis reactions

(57) The present invention describes the use of cationic vinylidene, allenylidene and higher cumulenylidene complexes of ruthenium or osmium as catalysts or catalyst precursors for olefin metathesis reactions of all types, as well as to new cationic allenylidene complexes of ruthenium and osmium which can be used as metathesis catalysts with preferred embodiment. These catalysts or catalyst precursors are easy to prepare from well accessible, stable and essentially non toxic starting materials, can be isolated and stored, they exhibit a high catalytic activity, a good compatibility with functional groups, solvents, water and additives, and they need not to be activated by any additive. Olefins of all types can be used as the substrates in the present invention in ring closing metathesis (RCM) of acyclic dienes and polyenes, the metathesis of enynes and dienynes, the ring opening metathesis polymerization (ROMP) of cyclic olefins, the acyclic diene metathesis polymerization (ADMET) of acyclic dienes or polyenes, the depolymerization of olefinic polymers, and the cross metathesis of two or more olefins. The present invention also applies to combinations of these types of metathetic reactions and domino processes thereof.

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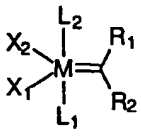
Description

BACKGROUND OF THE INVENTION

[0001] The present invention describes the use of cationic vinylidene, allenylidene and higher cumulenylidene complexes of ruthenium or osmium as catalysts or catalyst precursors for olefin metathesis reactions of all types. The present invention also relates to new cationic allenylidene complexes of ruthenium and osmium which can be used as metathesis catalysts with preferred embodiment. These catalysts or catalyst precursors are easy to prepare from well accessible, stable and essentially non toxic starting materials, can be isolated and stored, they exhibit a high catalytic activity, a good compatibility with functional groups, solvents, water and additives, and they need not to be activated by any additive. Olefins of all types can be used as the substrates in the present invention.

PRIOR ART

[0002] Olefin metathesis refers to the interchange of carbon atoms between a pair of double bonds. Reactions of this type have found applications to processes of industrial importance (Reviews: Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*, Academic Press, New York, **1997**; Schuster, M. et al., *Angew. Chem.* **1997**, *109*, 2125). Olefin metathesis reactions are catalyzed by various metal compounds. Many of the classical catalysts consist of mixtures of various components, they are ill defined in their chemical composition, show a poor compatibility with functional groups and are inefficient as a consequence of little active species present. More modern catalysts or catalyst precursors with a better application profile comprise complexes of the general types **I-IX**: (references: type **I** (M = Ru, Os): **WO** 96/04289, 15.02.1996; Nguyen S.T. et al. *J. Am. Chem. Soc.* **1992**, *114*, 3974; Nguyen S.T. et al. *J. Am. Chem. Soc.* **1993**, *115*, 9858; Schwab, P. et al. *Angew. Chem.* **1995**, *107*, 2179 (*Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 2039); Schwab, P. et al. *J. Am. Chem. Soc.* **1996**, *118*, 100; Mohr, B. et al. *Organometallics* **1996**, *15*, 4317; Wilhelm, T. E. et al. *Organometallics* **1997**, *16*, 3867; Belderrain, T. R. *Organometallics* **1997**, *16*, 4001. Type **II** (M = Mo, W): Schrock, R. R. et al. *J. Am. Chem. Soc.* **1990**, *112*, 3875; Fujimura, O. et al. *Organometallics* **1996**, *15*, 1865. Type **III**: Quignard, F. et al. *J. Mol. Catal.* **1986**, *36*, 13. Type **IV** (M = Nb, Ta): Rocklage, S. M. et al. *J. Am. Chem. Soc.* **1981**, *103*, 1440; Wallace, K. C. et al. *Macromolecules* **1987**, *20*, 448. Type **V** (cp = cyclopentadienyl or substituted cyclopentadienyl): **US** 4,567,244, 28.01.1986. Type **VI**: Herrmann, W. A. et al. *Angew. Chem.* **1991**, *103*, 1704. Type **VII**: Nugent, W. A. et al. *J. Am. Chem. Soc.* **1995**, *117*, 8992. Type **VIII**: Davie, E. S. *J. Catal.* **1972**, *24*, 272. Type **IX**: Herrmann, W. A. et al. *Angew. Chem.* **1996**, *108*, 1169.)



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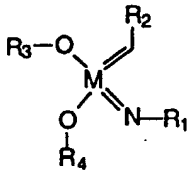

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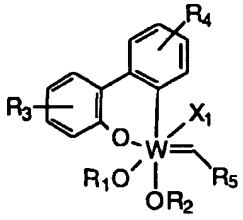

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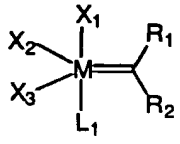

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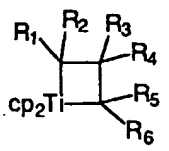


V

R_1-ReO_3

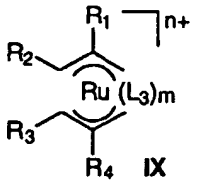
VI

$WO(X_1)_2(OR_1)_2/PbEt_4$

VII

$Mo(CO)_6/Al_2O_3$

VIII



IX

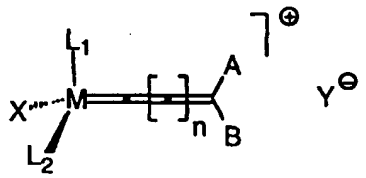
[0003] A major disadvantage of these complexes relates to their preparation which requires either reagents which are hazardous (e. g. type I: diazoalkanes), or difficult to prepare (e. g. type I: diphenylcyclopropene), or extremely sensitive (e. g. type II, III, IV, V, VI). Another disadvantage relates to the fact that some of these metathesis catalysts themselves are very sensitive to oxygen, moisture and/or polar functional groups and must be handled with great care under a strictly inert athmosphere (e. g. types II, III, IV, V). Another disadvantage relates to the fact that some of these complexes exhibit a reasonable reactivity only after activation with an additive, which can either be hazardous (e. g. for type IX: diazoalkanes) or toxic (e. g. for type VII: $PbEt_4$). Catalysts of type VI are active only when deposited on special oxidic supports.

Therefore a stringent need for metathesis catalysts persists, which reach or surpass the activity of the best catalysts I-IX described to date, but which are more readily accessible, require no hazardous reagents for their preparation, are robust, easy to isolate and handle, and need not be activated by any hazardous or toxic additives.

DETAILED DESCRIPTION OF THE INVENTION

[0004] The present invention meets the criteria mentioned above. Surprisingly we find that cationic vinylidene, allenylidene and higher cumulenylidene complexes of ruthenium or osmium are highly efficient catalysts or catalyst precursors for olefin metathesis reactions of all types. These catalysts or catalyst precursors are easy to prepare from well accessible, stable and essentially non toxic starting materials, can be isolated and stored, they exhibit a high catalytic activity, a good compatibility with functional groups, solvents, water and additives, and they need not to be activated by any additive. Of the catalysts mentioned above, compounds of the general type XII, as specified below, are new compounds.

[0005] Specifically, the present invention relates to the use of vinylidene, allenylidene and higher cumulenylidene complexes of the general formula X as catalysts in olefin metathesis reactions of all types



X

wherein

- M is Ru or Os;
- X can be selected from any anionic ligand;
- L_2 can be selected from any type of phosphine, sulfonated phosphine, fluorinated phosphine, functionalized phosphine bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl-, ketoalkyl- groups, phosphite, phosphinite, phosphonite, arsine, stibene.
- L_1 can be selected from any neutral π-bond ligand, preferably arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;
- A, B can be independently selected from hydrogen or a hydrocarbon from the group consisting of C1-C20 alkyl, aryl, C2-C20 alkenyl, alkynyl, C1-C20 alkoxy, carboxylate, carbamate, C2-C20 alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, C1-C20 alkylthio, alkylsulfonyl, alkylsulfinyl, arylthio, arylsulfonyl, arylsulfinyl, alkylamido, alkylamino, each of which may be substituted with C1-C10 alkyl, perfluoroalkyl, aryl, alkoxy or with halogen;
- Y may be selected from any non-coordinating anion;
- n is 0-5;

in a preferred embodiment:

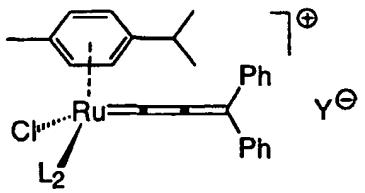
- M is Ru or Os
- X is halogen
- L_2 is selected among phosphines bearing one or more secondary alkyl, tertiary alkyl, or cycloalkyl groups, preferably P(isopropyl)$_3$, P(cyclohexyl)$_3$, P(cyclopentyl)$_3$, P(neopentyl)$_3$, P(tertiobutyl)$_3$.
- L_1 is benzene or a substituted benzene derivative bearing up to six substituents which may be identical or not iden-

tical and can be independently selected from C1-C20 alkyl, aryl, alkoxy, aryloxy, alkylsulfonyl, arylsulfonyl, perfluoroalkyl, alkylthio, alkenylthio, C2-C10 alkenyl, alkynyl, alkenyloxy, alkynyloxy, or halogen, most preferably L_1 is toluene, xylene, cymene, trimethylbenzene, tetramethylbenzene, hexamethylbenzene, tetraline, naphthalene, or polycyclic arenes and their derivatives.

Y is selected from PF_6^-, BF_4^-, BPh_4^-, $F_3CSO_3^-$, $H_3CSO_3^-$, ClO_4^-, SO_4^-, NO_3^-, PO_4^-, CF_3COO^-, $B(C_6F_5)_4^-$, RSO_3^-, $RCOO^-$ with R being selected from C1-C20 alkyl, aryl

n is 1.

[0006] The most preferred catalysts of the present invention include **XI**



XI

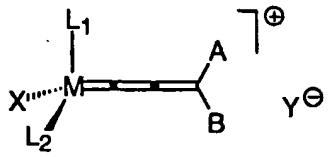
wherein

L_2 can be selected from P(isopropyl)$_3$, P(cyclohexyl)$_3$, P(cyclopentyl)$_3$, P(neopentyl)$_3$, P(tertiobutyl)$_3$

Y is selected from PF_6^-, BF_4^-, BPh_4^-, $F_3CSO_3^-$, $H_3CSO_3^-$, ClO_4^-, SO_4^-, NO_3^-, PO_4^-, CF_3COO^-, $B(C_6F_5)_4^-$, RSO_3^-, $RCOO^-$ with R being selected from C1-C20 alkyl, aryl

[0007] The preparation of these catalysts can be achieved by following the approach described in: Pilette, D. et al., *Organometallics* **1992**, *11*, 809.

[0008] The present invention also relates to new compounds of the general type **XII**



XII

wherein

M is Ru or Os

X can be selected from any anionic ligand;

L_1 can be selected from any neutral π-bond ligand, preferably arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L_2 is selected among phosphines, arsine or stibenes bearing one or more secondary alkyl, tertiary alkyl, or cycloalkyl groups;

A, B can be independently selected from hydrogen or a hydrocarbon from the group consisting of C1-C20 alkyl, aryl, C2-C20 alkenyl, alkynyl, C1-C20 alkoxy, carboxylate, carbamate, C2-C20 alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, C1-C20 alkylthio, alkylsulfonyl, alkylsulfinyl, arylthio, arylsulfonyl, arylsulfinyl, alkylamido, alkylamino, each of which may be substituted with C1-C10 alkyl, perfluoroalkyl, aryl, alkoxy or with halogen;

Y may be selected from any non-coordinating anion.

[0009] Compounds of the general type **XII** can be used as catalysts for olefin metathesis reactions according to the

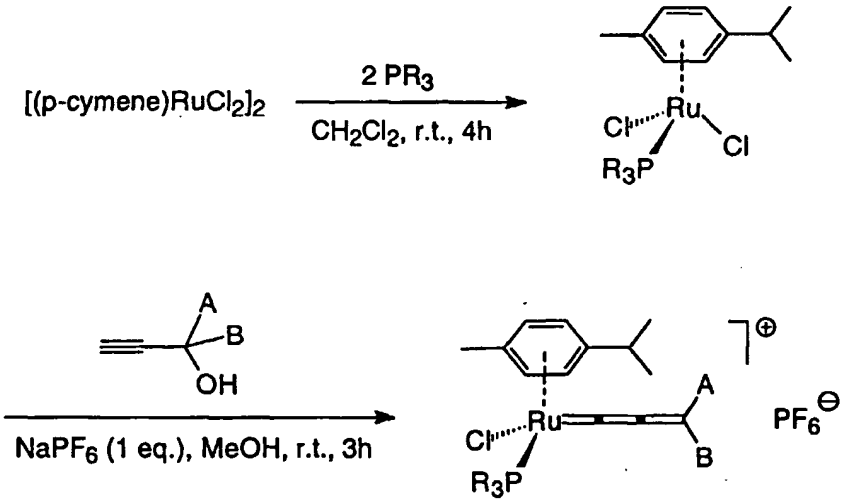
present invention. In a preferred embodiment

M is Ru
X is halogen
L_1 is benzene or substituted benzene
L_2 is selected among phosphines, arsine or stibenes bearing one or more secondary alkyl, tertiary alkyl, or cycloalkyl groups
A, B can be independently selected from a hydrocarbon from the group consisting of C1-C20 alkyl, aryl,
Y may be selected from any non-coordinating anion.

[0010] Compounds of the general type **XII** can be used as most preferred catalysts for olefin metathesis reactions according to the present invention, wherein

M is Ru
X is chloride
L_1 is p-cymene
L_2 is selected among P(isopropyl)$_3$, P(cyclohexyl)$_3$, P(cyclopentyl)$_3$, P(neopentyl)$_3$, P(tertiobutyl)$_3$.
A, B are aryl or substituted aryl
Y may be selected from PF_6^-, BF_4^-, BPh_4^-, $F_3CSO_3^-$, $H_3CSO_3^-$, ClO_4^-, SO_4^-, NO_3^-, PO_4^-, CF_3COO^-, $B(C_6F_5)_4^-$, RSO_3^-, $RCOO^-$ with R being selected from C1-C20 alkyl, aryl.

[0011] The synthesis of compounds of the general type **XII** can be achieved according to Equation 1; examples for the preparation of compounds of the general type **XII** which serve as catalysts with most preferred embodiments according to the present invention are described in Examples 1 and 2. The ease of this preparation is a distinct advantage for the process of this invention over the processes of the prior art. Another major advantage relates to the fact that all hazardous, unstable and difficult to handle reagents are avoided which were previously used for the preparation of highly performing metathesis catalysts. This refers particularly to diazoalkanes and cyclopropene derivatives which are avoided in the catalysts used in the present invention. The fact that the cationic ruthenium or osmium complexes of the general type **X-XII** must not be activated by addition of diazoalkanes distinguishes them from other metathesis catalysts presently used, in particular from the cationic bisallylruthenium (+4) complexes of the general type **IX** previously described in the literature (Herrmann, W. A. et al. *Angew. Chem.* **1996**, *108*, 1169).



Equation 1. Example for the synthesis of a compound of the general type **XII** which can serve as metathesis catalyst according to the present invention.

[0012] It is not necessary to isolate and purify the catalyst precursor, but cationic complexes of the general type **X-XII**

outlined above may be prepared in situ and directly used in metathesis reactions.

[0013] Examples of the reactions induced by the catalysts mentioned above include, but are not limited to, the ring closing metathesis (RCM) of acyclic dienes and polyenes, the metathesis of enynes and dienynes, the ring opening metathesis polymerization (ROMP) of cyclic olefins, the acyclic diene metathesis polymerization (ADMET) of acyclic dienes or polyenes, the depolymerization of olefinic polymers, and the cross metathesis of two or more olefins. The present invention also applies to combinations of these types of metathetic reactions, to domino processes thereof (Tietze, L. F. et al. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131), and to the dimerization or oligomerization of dienes followed by subsequent ring closure (cyclodi[oligo]merization).

[0014] The present invention applies to all types of olefins, independent of whether they are cyclic or acyclic, strained or unstrained, as well as to mixtures of olefins. The substrates can be used in polymer supported form or can be successively added to the reaction mixture.

[0015] The reactions are usually carried out by contacting the olefin substrate (neat or in solution) with the catalyst and optionally heating the mixture until the reaction is complete. The temperatures can range from -20°C to about 150°C, preferably 10°C to 90°C. The reaction time is not critical and can be from a few minutes to several days. The reactions are generally carried out under inert atmosphere, most preferably nitrogen, argon or CO_2, but the presence of oxygen may be tolerated under certain circumstances. The reaction can be carried out under irradiation of the reaction mixture. The reaction can be performed in water or in the presence of water.

[0016] The ratio of catalyst to olefin substrate is not critical and can range from 1:5 to about 1:30000, preferably it is in the range of 1:20 to 1:2000.

[0017] Work-up of the reaction mixtures and purification is not critical and follows routine techniques depending on the specific properties of the products formed and/or the unreacted starting material. This may proceed either by distillation, filtration, chromatography, sublimation, crystallization, extraction as the preferred techniques.

[0018] Catalysts of the type described above are stable in the presence of a variety of functional groups, which include, but are not limited to, alcohol, acetal, ketal, keteneacetal, thiol, thioacetal, ketone, aldehyde, ester, ether, epoxide, gem-dialkyl group, amine, ammonium salt, amide, nitro, carboxylic acid, sulfide, disulfide, carbonate, carbamate, isocyanide, nitrile, urethane, urea, halogen, imine, sulfonate, sulfone, sulfoxide, silyl, stannyl, perfluoroalkyl, phosphonate, ferrocene, as well as oxygen-, nitrogen-, sulfur or phosphorous containing heterocycles.

[0019] In the case of ROMP, the present invention applies to the preparation of Vestenamer® (Dräxler, A. et al. *Der Lichtbogen* **1986**, *35*, 24) and Norsorex® (Ohm, R. F.; *Chemtech* **1980**, 183).

[0020] In the case of oligomerization and polymerization reaction of appropriate monomers, the propagating carbene moiety was found to be stable and continues to polymerize additional aliquots of monomer for a period after the original amount of monomer has been consumed. The added monomer may be identical or not identical to the original one.

[0021] In case of RCM, the catalysts mentioned above apply to the formation of all ring sizes $x \geq 5$, including medium sized ($8 \leq x \leq 11$) and large ($x \geq 12$) rings, independent of whether the rings are carbocyclic or heterocyclic; the newly formed ring may be anellated to one or more pre-existing aromatic or non-aromatic carbo- or heterocyclic rings. The invention applies, but is not restricted, to the synthesis of products which may be used as pheromones, crown ethers, antibiotics, agro chemicals, pharmaceuticals for human and veterinary medicine, fragrances, flavors, perfume ingredients. Representative examples are compiled in Table 1.

[0022] In the case of the formation of macrocyclic rings which serve as perfume ingredients, the present invention applies to the synthesis of pentadecanolide or homologues, Arova 16 or homologues, civetone or homologues, muscone or homologues, Exalton or homologues, muscenone or homologues, ethylenebrassylate (Musk 144) or homologues, and related macrocycles as described in Fürstner, A. et al., *Synthesis* **1997**, 792 and US Appl. 08/767.561 (16.12.1996).

[0023] In the case of the formation of medium or macrocyclic rings by RCM, the olefin substrates may be devoid of any conformational predisposition to ring closure as induced by various elements of structural preorganization.

[0024] Metathesis reactions catalyzed by the cationic vinylidene, allenylidene and higher cumulenylidene complexes of the general formula **X-XII** can be performed in any solvent or solvent mixture which does not inactivate the catalyst. This includes protic and aqueous solvents, compressed carbon dioxide (DE-A 19720798.7 (15.5.1997)), or perfluoroalkanes. However it is preferred to work under aprotic conditions in solvents with low coordination ability. Examples of preferred solvents include, but are not restricted to, dichloromethane, trichloromethane, 1,2-dichloroethane, trichloroethane, benzene, toluene, xylene, halobenzenes, cymene, tetrahydrofuran, diethylether, tert-butylmethylether, dimethoxyethane, petrol ether, hexane, cyclohexane, acetone. Depending on the specific physical properties of the substrates and products, the reactions can also be carried out with neat alkenes without any additional solvent added to the reaction mixture. Examples of cyclization reactions in preferred embodiments are given in Tables 1 and 2.

[0025] The concentration of the substrate (molarity, M) in a given solvent may be largely varied. Under certain circumstances the reaction can be carried out with neat substrates without any additional solvent. In the case of RCM leading to the formation of medium and macrocyclic rings it is preferred to work at molarities $M \leq 0.1$ in order to suppress the dimerization, cyclodimerization or polymerization of the diene substrates. In a preferred embodiment, solutions of the

substrate and of the catalyst are combined at such a rate that the propensity of cyclization of the respective substrate is greater than that of a reactive encounter of two substrate molecules.

[0026] As a result of their stability in the presence of functional groups, the catalysts may be employed in the presence of one or more additives. Examples include, but are not limited to, metal salts, metal alkoxides, Lewis acids, perfluoroalkanes, phosphorous compounds, detergents, surfactants, silica, alumina, graphite, $CaCO_3$, or aluminum powder.

Table 1. RCM using catalyst (*p*-cymene)RuCl(PCy_3)(=C=C=CPh_2)$^+PF_6^-$ (2-5 mol%) in toluene at 80°C.

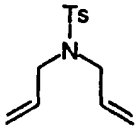
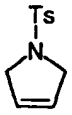
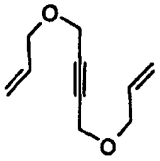
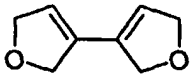
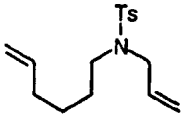
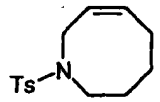
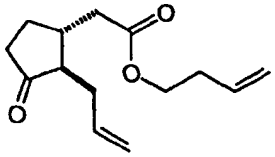
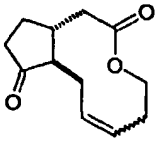
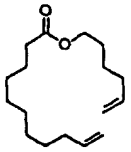
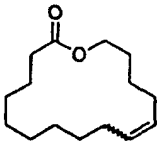
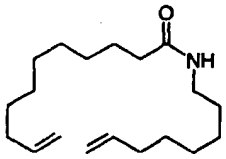
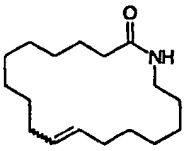
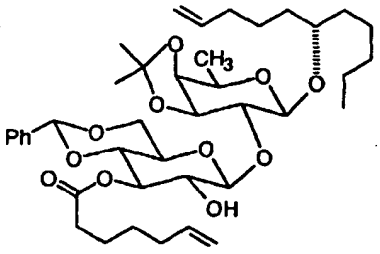
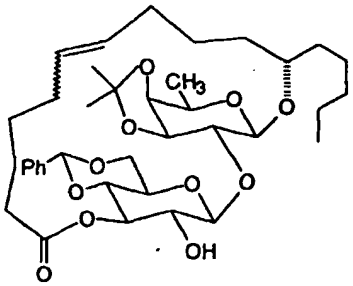
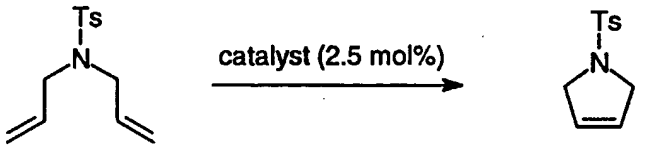
Substrate	Product	Yield
		83%
		86%
		75%
		40%
		90%
		55%
		85%

Table 2. Cyclization reactions under various conditions using two different catalysts with most preferred embodiments:

A: (*p*-cymene)RuCl($PiPr_3$)(=C=C=CPh_2)$^+PF_6^-$;

B: (*p*-cymene)RuCl(PCy_3)(=C=C=CPh_2)$^+PF_6^-$



Catalyst	Solvent	Additive	T (°C)	t (h)	Yield (%)[a]
A	toluene	—	80	3	66
A	CH_2Cl_2	---	40	26	95 (76)
B	toluene	---	80	3	79
B	toluene	---	80	4	100 (83)
B	toluene	cymene (50%)	80	3	47
B	toluene	PCy_3 (5%)	80	3	31

[a] GC-yield (isolated yield).

EXAMPLES

[0027] Abbreviations used: Cy = cyclohexyl; iPr = isopropyl; Ph = phenyl

[0028] The following prototype examples set forth the synthesis of catalysts and olefin metathesis reactions in preferred embodiments of the present invention. Further objectives and advantages of the present invention not mentioned above will become appearant from the examples which are not intended to limit its scope.

EXAMPLE 1

[0029] **(*p*-Cymene)RuCl(PCy_3)(=C=C=CPh_2)$^+PF_6^-$.** In a Schlenk tube under argon are loaded $NaPF_6$ (0.099 g, 0.589 mmol, 1 eq.), the complex (*p*-cymene)$RuCl_2(PCy_3)$ (0.344 g, 0.586 mmol) [prepared according to: Zelonka R. A. et al. *Can. J. Chem.* **1972**, *50*, 3063; Demonceau A. et al. *Macromolecules* **1997**, *30*, 3127], 1,1-diphenylprop-2-yn-1-ol (0.0243 g, 1.168 mmol, 2 eq.) and 30 ml of MeOH. The solution is stirred 3 h at room temperature, then the solvent is evaporated. The diphenylpropynol in excess is eliminated by washing the residue with 2x20 ml of Et_2O. The complex is then extracted with 2x10 ml of CH_2Cl_2 (separation from NaCl formed during the reaction), and the solution is evapo-

rated. The violet powder obtained is washed again with 20 ml of Et_2O, filtered and dried under vacuum. Violet powder (97 %). ^{31}P NMR ($CDCl_3$, 81.015 MHz) d (ppm): 58.81 (PCy_3); -140.80 (sp, J_{PF} = 40 Hz, PF_6^-); ^1H NMR ($CDCl_3$, 200.132 MHz) d (ppm): 7.87 (md, 4 H, J= 7.2, Ph); 7.75 (m, 2 H, Ph); 7.48 (m, 4 H, Ph); 6.63 (md, 1 H, J= 6.6, H arom p-cym.); 6.47 (md, 1 H, J= 6.5, H arom p-cym.); 6.11 (md, 1 H, J= 6.7, H arom p-cym.); 6.02 (md, 1 H, J= 5.9, H arom p-cym.); 2.72 (hept, 1 H, CH iPr p-cym.); 2.20 (m broad, 3 H, cyclohexyl H-1); 2.20 (s, 3 H, Me); 1.29 (m, 6 H, CH_3 iPr p-cym.); 2.1-0.9 (m, 30 H, cyclohexyl); IR (KBr, ν cm^{-1}): 3057, 3026 (=CH); 2932, 2854 (C-H); 1959 (Ru=C=C=C); 1594, 1490, 1448 (Ph); 840, 557 (PF_6^-); Calcd. for $C_{34}H_{45}ClF_6P_2Ru$: C, 53.30; H, 5.92; P, 8.09. Found: C, 52.19; H, 5.73; P, 8.05%.

EXAMPLE 2

[0030] **(*p*-Cymene)RuCl(PiPr$_3$)(=C=C=CPh$_2$)$^+$PF$_6^-$.** Following the procedure described in example 1 with 0.043 g of $NaPF_6$ (0.256 mmol, 1 eq.), 0.117 g of the complex (*p*-cymene)$RuCl_2(PiPr_3)$ (0.251 mmol, 1 eq.), 0.063 g of 1,1-diphenylprop-2-yn-1-ol (0.302 mmol, 1.2 eq.) and 15 ml of MeOH in 4 h at room temperature. The diphenylpropynol in excess is eliminated by washing the residue with 10 ml of Et_2O. The complex is then washed with 3x20 ml of toluene and extracted with 20 ml of CH_2Cl_2. Violet powder, 95%. ^{31}P NMR ($CDCl_3$, 81.015 MHz) d (ppm): 68.14 ($PiPr_3$); -143.69 (sp, $^1J_{PF}$ =40.75 Hz, PF_6^-); ^1H NMR ($CDCl_3$, 200.132 MHz) d (ppm): 7.86 (md, 4 H, J= 7.1, Ph); 7.75 (m, 2 H, Ph); 7.48 (m, 4 H, Ph); 6.62 (md, 1 H, J= 6.9, H arom p-cym.); 6.54 (md, 1 H, J= 6.9, H arom p-cym.); 6.09 (m, 2 H, H arom p-cym.); 3.05-2.50 (m, 4 H, CH iPr.); 2.33 (s, 3 H, CH_3 p-cym.); 1.51 (d, 3 H, J= 7.2 CH_3 iPr p-cym.); 1.42 (d, 3 H, J= 7.2 CH_3 iPr p-cym.); 1.35-1.10 (m, 18 H, CH_3 P(iPr)$_3$); IR (KBr, ν cm^{-1}): 3058 (=CH); 2967, 2932, 2876 (C-H); 1945 (Ru=C=C=C); 1587, 1487 (Ph); 839, 557 (PF_6^-); MS: 621.2 (M+-PF_6).

EXAMPLE 3

[0031] **N-Tosyl-2,5-dihydropyrrole.** A solution of N,N-diallyltosylamide (259 mg, 1.03 mmol) and the allenylidene complex (*p*-cymene)RuCl(PCy_3)(=C=C=CPh$_2$)$^+$PF$_6^-$(22 mg, 0.0248 mmol, 2.4 mol%) in toluene (5 mL) is stirred for 4 h at 80 °C. The solvent is evaporated and the crude product purified by flash chromatography using ether : pentane (1 : 4) as the eluent. This affords the title compound as a colorless solid (191 mg, 83%). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 4.10 (s, 4H), 5.63 (s, 2H), 7.30 (dm, 1H, *J* = 8.6, 0.7), 7.70 (dm, 1H, *J* = 8.3, 1.9). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.1, 54.5, 125.1, 129.3, 129.4, 139.2, 143.1. IR (KBr): 3093, 3047, 2951, 2909, 2854, 1928, 1817, 1595, 1540. MS (rel. Intensity): 223 (28, [M$^+$]), 155 (28), 91 (72), 68 (100), 41 (19). $C_{11}H_{13}NO_2S$ (223.3): *calcd.* C 59.17, H 5.83, N 6.27, S 14.36; *found* C 59.26, H 5.91, N 6.22, S 14.36.

EXAMPLE 4

[0032] **N-Tosyl-2,5-dihydropyrrole.** A solution of N,N-diallyltosylamide (259 mg, 1.03 mmol) and the allenylidene complex (*p*-cymene)RuCl(PiPr$_3$)(=C=C=CPh$_2$)$^+$PF$_6^-$(22 mg, 0.0248 mmol, 2.4 mol%) in CH_2Cl_2 (5 mL) is refluxed for 26 h under argon. The solvent is evaporated and the crude product purified by flash chromatography using ether: pentane (1 : 4) as the eluent. This affords the title compound as a colorless solid (76%), the spectral data of which are identical to those reported above.

EXAMPLE 5

[0033] **Pentadec-10-enolide.** Solutions of 5-hexen-1-yl 10-undecenoate (134 mg, 0.503 mmol) and complex (*p*-cymene)RuCl(PCy_3)(=C=C=CPh$_2$)$^+$PF$_6^-$ (22 mg, 0.0248 mmol, 4.9 mol%) in toluene (50 mL each) are added over a period of 24 h *via* two dropping funnels to toluene (25 mL) at 80°C. Stirring is continued for another 16 h at that temperature prior to evaporation of the solvent and purification of the residue by flash chromatography using ether : pentane (1 : 20) as the eluent. This affords the macrocycle as a colorless syrup (108 mg, 90%). ^1H NMR (200 MHz, $CDCl_3$): δ = 5.45-5.28 (m, 2H), 4.18-4.07 (m, 2H), 2.37-2.29 (m, 2H), 2.10-2.00 (m, 4H), 1.72-1.54 (m, 4H), 1.49-1.30 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.9, 131.7, 130.4, 130.1, 129.6, 64.1, 64.0, 34.7, 33.9, 32.0, 29.1, 28.4, 28.4, 28.3, 28.2, 28.1, 28.0, 27.9, 27.6, 27.2, 27.1, 26.6, 26.5, 25.4, 25.2. IR (KBr): 3000, 2928, 2856, 1736, 1461, 1385, 1346, 1252, 1234, 1168, 1152, 1113, 1085, 1024, 969, 719. MS (rel.Intensity): 238 ([M$^+$], 20), 210 (18), 109 (17), 96 (49), 82 (100), 67 (64), 55 (64). $C_{15}H_{26}O_2$ (228.37): *calcd.* C 75.58, H 10.99; *found* C 75.65, H 11.08.

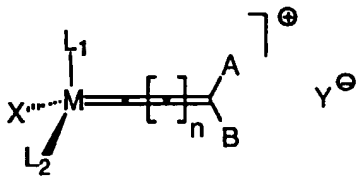
EXAMPLE 6

[0034] **3-(2,5-Dihydrofuran-3-yl)-2,5-dihydrofuran.** A mixture of 1,4-bis(allyloxy)-2-butyne (157 mg, 1.02 mmol) and (*p*-cymene)RuCl(PCy_3)(=C=C=CPh$_2$)$^+$PF$_6^-$ (22 mg) in toluene (5 mL) is stirred for 3 h under argon at 80°C. The solvent

is evaporated and the residue purified by flash chromatography using diethylether/pentane (1/4) as eluent. This affords the title compound as white solid (110 mg, 86%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.70 (br. S, 8H), 5.59 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 74.7, 76.0, 122.5, 131.4.

Claims

1. A process for metathesis reactions of all types, comprising contacting an olefin with a catalyst, wherein the catalyst comprises vinylidene, allenylidene and higher cumulenylidene complexes of the general formula



wherein

M	is Ru or Os;
X	can be selected from any anionic ligand;
L_2	can be selected from any type of phosphine, sulfonated phosphine, fluorinated phosphine, functionalized phosphine bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl-, ketoalkyl- groups, phosphite, phosphinite, phosphonite, arsine, stibene.
L_1	can be selected from any neutral π-bond ligand, preferably arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;
A and B	can be independently selected from hydrogen or a hydrocarbon from the group consisting of C1-C20 alkyl, aryl, C2-C20 alkenyl, alkynyl, C1-C20 alkoxy, carboxylate, carbamate, C2-C20 alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, C1-C20 alkylthio, alkylsulfonyl, alkylsulfinyl, arylthio, arylsulfonyl, arylsulfinyl, alkylamido, alkylamino, each of which may be substituted with C1-C10 alkyl, perfluoroalkyl, aryl, alkoxy or with halogen
Y	may be selected from any non-coordinating anion;
n	is 0-5.

2. The process according to claim 1, in which the catalyst is prepared in situ and used in metathesis reactions without prior isolation.

3. The process according to claims 1 or 2, in which the olefin may be cyclic or acyclic with or without one or more functional groups; said functional groups comprise alcohol, acetal, ketal, keteneacetal, thiol, thioacetal, ketone, aldehyde, ester, ether, epoxide, gem-dialkyl group, amine, ammonium salt, amide, nitro, carboxylic acid, sulfide, disulfide, carbonate, carbamate, isocyanide, nitrile, urethane, urea, halogen, imine, sulfonate, sulfone, sulfoxide, silyl, stannyl, perfluoroalkyl, phosphonate, ferrocene, as well as oxygen-, nitrogen-, sulfur or phosphorous containing heterocycles.

4. The process according to claims 1-3, in which the olefins are bound to a polymer.

5. The process according to claims 1-3, in which the reaction is carried out in the absence of solvents with neat alkenes.

6. The process according to claims 1-5, in which the reaction is carried out in a solvent or solvent mixture which does not inactivate the catalyst.

7. The process according to claims 1-6, which is carried out in the presence of additives; said additives comprise metal salts, metal alkoxides, Lewis acids, perfluoroalkanes, phosphorous compounds, detergents, surfactant, silica, alumina, graphite, $CaCO_3$, or aluminum powder.

8. The process according to claims 1-7, in which the reaction is carried out under irradiation of the reaction mixture.

9. The process according to claims 1-8, in which the metathesis reaction leads to cyclic products of any ring size $x \geq 5$ by ring closing olefin metathesis (RCM), enyne metathesis, metathesis depolymerization reactions, or combinations or domino processes thereof, independent of whether the product is carbocyclic or heterocyclic.

10. The process according to claim 9, in which the products are anellated to one or more pre-existing aromatic or non-aromatic carbo- or heterocyclic rings.

11. The process according to claims 9-10, in which the cyclic products are medium sized ($8 \leq x \leq 11$) and macrocyclic ($x \geq 12$) rings.

12. The process according to claims 9-11, wherein the cyclic products are used as pheromones, crown ethers, antibiotics, agro chemicals, pharmaceuticals for human and veterinary medicine, fragrances, flavors, or perfume ingredients.

13. The process according to claim 12, wherein the products used as perfume ingredients comprise pentadecanolide or homologues, Arova 16 or homologues, civetone or homologues, muscone or homologues, Exalton or homologues, muscenone or homologues, ethylenebrassylate (Musk 144) or homologues as well as related macrocycles.

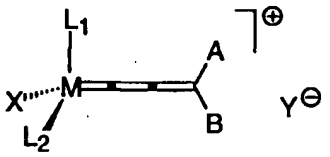
14. The process according to claims 1-8, in which the metathesis reactions afford polymeric products by ring opening metathesis polymerization (ROMP) of strained or unstrained cyclic olefin monomers or by acyclic diene metathesis polymerization (ADMET).

15. The process according to claim 14, in which the polymeric products are produced by addition of monomers to the reaction mixture after the original amount of monomer has been consumed; said added monomer can be identical or not identical to the original one.

16. The process according to claims 14-15, in which the polymeric products are Vestenamer and Norsorex.

17. The process according to claims 1-8, wherein the metathesis reaction is a cross metathesis of two or more olefins.

18. A compound of the general type **XII**



XII

wherein

M	is Ru or Os;
X	can be selected from any anionic ligand;
L_1	can be selected from any neutral π-bond ligand, preferably arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;
L_2	is selected among phosphines, arsine or stibenes bearing one or more secondary alkyl, tertiary alkyl, or cycloalkyl groups
A, B	can be independently selected from hydrogen or a hydrocarbon from the group consisting of C1-C20 alkyl,

aryl, C2-C20 alkenyl, alkynyl, C1-C20 alkoxy, carboxylate, carbamate, C2-C20 alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, C1-C20 alkylthio, alkylsulfonyl, alkylsulfinyl, arylthio, arylsulfonyl, arylsulfinyl, alkylamido, alkylamino, each of which may be substituted with C1-C10 alkyl, perfluoroalkyl, aryl, alkoxy or with halogen;

Y⁻ may be selected from any non-coordinating anion.

19. A compound according to claim 18, wherein

M is Ru
X is halogen
L_1 is benzene or substituted benzene
L_2 is selected among phosphines, arsine or stibenes bearing one or more secondary alkyl, tertiary alkyl, or cycloalkyl groups
A, B can be independently selected from a hydrocarbon from the group consisting of C1-C20 alkyl, aryl,
Y⁻ may be selected from any non-coordinating anion.

20. A compound according to claim 19, wherein

M is Ru
X is chloride
L_1 is p-cymene
L_2 is selected among $P(isopropyl)_3$, $P(cyclohexyl)_3$, $P(cyclopentyl)_3$, $P(neopentyl)_3$, $P(tertiobutyl)_3$.
A, B are aryl or substituted aryl
Y⁻ may be selected from PF_6^-, BF_4^-, BPh_4^-, $F_3CSO_3^-$, $H_3CSO_3^-$, ClO_4^-, SO_4^-, NO_3^-, PO_4^-, CF_3COO^-, $B(C_6F_5)_4^-$, RSO_3^-, $RCOO^-$ with R being selected from C1-C20 alkyl, aryl.

21. The process according to claims 1-17, wherein the catalysts comprise compounds of the general formula **XII**.

22. A method for the preparation of compounds of the general formula **XII** comprising a condensation of (arene)$RuCl_2(PR_3)$ and alkynols HC≡C-C(OH)AB or derivatives thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 12 1228

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 97 06185 A (CALIFORNIA INST OF TECHN) 20 February 1997 * page 3, line 32 - page 4, line 11 *	1,18,21	C07F15/00 B01J31/22 C07C6/04
D,A	WO 96 04289 A (CALIFORNIA INST OF TECHN) 15 February 1996		
A	WO 93 20111 A (DU PONT ;CALIFORNIA INST OF TECHN (US)) 14 October 1993		
A	DE 44 47 066 A (HOECHST AG) 4 July 1996		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C07F
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 1998	Thion, M

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